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TITLE: Resolution of Cyclic Bases by Means of Bromcyanogen (II)

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GI For diagram(s), see printed CA Issue.

AB cf. C. A., 2, 118. Piperidocyanamide and p-toluidine hydrochloride, at 160°, form the guanidine derivative, C<sub>5</sub>H<sub>10</sub>NC(:NH)NHC<sub>6</sub>H<sub>4</sub>Me; crystalline, m. 115°. Picrate, m. 132°. Chloroplatinate, m. and evolves gas 205°. Phenyl derivative, from PhNH<sub>2</sub>; brittle crystalline mass. Picrate, m. about 107°. Chloroplatinate, orange-red, m. 195°. Dipiperido compound, C<sub>5</sub>H<sub>10</sub>NC(:NH)NC<sub>5</sub>H<sub>10</sub>, from piperidine hydrobromide and also from bromocyanogen and piperidine, without a solvent; colorless liquid with a slight basic odor, b<sub>12</sub> 175-7°. Picrate, well developed, yellow needles, m. 148°. Chloroplatinate, m. 192-200°, according to the rapidity of heating. γ-Phenoxypropylpiperidine, C<sub>5</sub>H<sub>10</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OPh, is easily prepared from piperidine and iodopropyl phenyl ether. Hydriodide, m. 183°. Methiodide, m. 159-60°. Bromocyanogen reacts with it to form cyanopiperidine, bromopropyl phenyl ether, .vepsiln.-bromamyl-γ-phenoxypropylcyanamide and piperidocyanamide. The first of these, together with phenoxypropylpiperidine, its hydrobromide and bromcyanogen are extracted by means of dilute acid, the other 3 are dissolved out by Et<sub>2</sub>O. The residue, after distillation of the Et<sub>2</sub>O, was subjected to the reactions described below. (I) When heated with fuming HBr, at 105-7°, piperidine hydrobromide, trimethylene bromide and .vepsiln.-bromoamyl-γ-bromopropylcyanamide, BrCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>N(CN)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, are produced. Colorless oil which could not be distilled. Yield, about 50%. (2) Sodium phenolate forms piperidine cyanide, trimethyleneglycoldiphenyl ether (PhOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, and the cyanamide, PhOCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>N(CN)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OPh, which are separated by fractional distillation. Crystalline, m. 36°; b<sub>10</sub> 100-30°. Yield, about 60%. (3) Condensation with piperidine leads to the formation of piperidocyanamide, phenoxypropylpiperidine, and piperidylcyanophenoxypropylpentamethylenediamine. The second of these, PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>5</sub>H<sub>10</sub>, is a pale yellow liquid with a basic odor. Its salts are oily. Picrate, chloraurate, chloroplatinate. Methiodide, plates. With HBr it gives the compound BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC<sub>5</sub>H<sub>10</sub>. Salts oily. Yield of the phenoxy compound 50%. (4) Methylaniline forms cyan piperidine, methylphenylcyanamide. Methylphenylcyanophenoxypropylpentamethylenediamine, PhNMeCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>N(CN)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OPh, and phenoxypropylmethylaniline, PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMePh; oil, b<sub>10</sub> 217°. Picrate, yellow plates, m. 111°. The diamine is a viscid, yellowish red, odorless liquid, b<sub>10</sub> 300-25°. Its salts crystallize with difficulty. (5) Aniline gives sym. diphenylguanidine, phenylcyanophenoxypropylpentamethylenediamine, PhNHCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>NMeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OPh, and phenoxypropylaniline. Hydrochloride, crystalline, m. 165°. Benzoyl derivative, m. 120°. The diamine mentioned above is a viscid, yellowish red liquid, b<sub>10</sub> 300-20°. All its derivatives are oily. (6) Potassium cyanide gives γ-phenoxybutyric nitrile and phenoxy .vepsiln.-leucine nitrile, NCCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>N(CN)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NOPh; oil, b<sub>15</sub> 230-60°. When hydrolyzed it yields the acid, PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(CN)CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H; colorless, m. 131°. (7) Potassium phthalimide reacts readily, but

the products could not be separated. N-Propylpiperidine and bromocyanogen form piperidinecyanamide, propyl bromide, .vepsiln.-bromamylpropylcyanamide and piperidylcyanopropylpentamethylenediamine,  $C_5H_{10}NCH_2(CH_2)_3CH_2N(CN)C_3H_7$ ; yellow, viscid liquid with a slightly basic odor, b<sub>9</sub> 196°. Picrate and methiodide, oily. It is hydrolyzed to the diamine,  $C_5H_{10}NCH_2(CH_2)_3CH_2NHC_3H_7$ ; water-clear, mobile liquid, b<sub>12</sub> 146-50°. Picrate, lustrous crystals, m. 175°. Chloroplatinate, orange-red, m. and decomposes 228°. Methiodide, benzenesulphonyl and benzoyl derivatives, oily. Ethyl  $\beta$ -piperidopropionate,  $C_5H_{10}NCH_2CH_2CO_2Et$ , b. 230°, not 218° as stated by Wedekind. Picrate, long, yellow crystals, m. 127°. Methiodide, oily. With bromocyanogen the chief product is the original ester hydrobromide (43%); apparently some ethyl acrylate is also formed. The remaining material was condensed with piperidine; the products of the reaction which were identified were dipiperidylguanidine, cyanopiperidine and piperidocyanamide.  $\gamma$ -Phthalimidopropylpiperidine, formula (I) below, is a colorless, crystalline powder, m. 50°. Picrate, m. 190°. With bromocyanogen there are formed piperidocyanamide,  $\gamma$ -bromopropylphthalimide, and a bromo derivative, probably (II); pale yellow, very viscid oil. N-Ethylpiperidine and bromocyanogen form N-ethylpiperidine hydrobromide, cyanopiperidine, EtBr and .vepsiln.-bromethylcyanamide. This last was separated by condensation with piperidine to piperidylcyanethylpentamethylenediamine,  $C_5H_{10}NCH_2(CH_2)_3CH_2NEtCN$ ; viscid, slightly colored liquid, b<sub>11</sub> 191-2°. Yield, about 50% of the ethylpiperidine. Picrate, oil. At 140°, with HCl, 70% of the base is hydrolyzed to piperidylethylpentamethylenediamine,  $C_5H_{10}NCH_2(CH_2)_3CH_2NH_2$ ; colorless liquid, b<sub>10</sub> 132°. Picrate, reddish yellow crystals, m. 151°. Chloroplatinate, orange-red, crystalline powder, m. 220°. Diethyl sodiomalonate and (II) condense to form a mixture of substances, which could not be distilled. When hydrolyzed with HCl, or HBr, at 180°, there are formed butyric acid, piperidine and  $\zeta$ -ethylaminoheptylic acid,  $EtNHCH_2(CH_2)_4CH_2CO_2H$ ; colorless solid, m. 129-30°. Benzenesulphonyl derivative, oily. Chloroplatinate, m. 117°. The acid easily becomes yellow when heated and passes into an anhydride. By the interaction of piperidoacetonitrile and bromocyanogen the ratio of formation of cyanopiperidine to the pentamethylene derivative is about 3:1, in the case of ethylpiperidine it is 2:1 and with propylpiperidine 2:3.

IT 32599-03-4, Piperidine, 1-( $\gamma$ -phenoxypropyl)-  
(derivs.)

RN 32599-03-4 CAPLUS

CN Piperidine, 1-(3-phenoxypropyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)

